PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-339620
(43)Date of publication of application : 13.12.1994

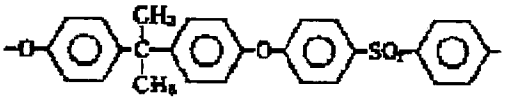
(51)Int.Cl. B01D 71/68
C08J 7/00
C08J 7/00

(21)Application number : 05-298075
(22)Date of filing : 29.11.1993

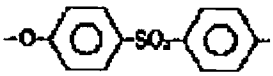
(71)Applicant : TORAY IND INC
(72)Inventor : SHIMAGAKI MASAAKI
TANAKA KAZUSANE
SHIMAMURA SEIJI

(54) METHOD FOR TREATING POLYSULFONE RESIN SEMIPERMEABLE MEMBRANE

(57)Abstract:
PURPOSE: To obtain a semi-permeable membrane with no eluation of blended polymers and high water permeability by applying radiation treatment on a polysulfone resin semi-permeable membrane and thereby corsslinking a hydrophilic polymer.
CONSTITUTION: Radiation treatment is applied on a polysulfone resin semi-permeable membrane prepd. by using a system wherein an additive being a non-solvent or a swelling agent to the polysulfone resin is added into a soln, prepd. by mixing and dissolving a polysulfone resin and a hydrophilic polymer, as a film- forming stock soln. to crosslink the hydrophilic polymer. The polysulfone resin ordinally consists of a repeating unit of formula I or II but it may contain a functional group or it may be an alkyl type. As the hydrophilic polymer, polyvinyl pyrrolidone is the best and modified polyvinyl pyrrolidone, polyethylene glycol etc., can be cited. As the solvent, dimethylacetamide, dimethyl sulfoxide, dimethylformamide, N-methyl-2-pyrrolidone are especially pref. As the additive, water is most pref. from the view point of production cost.



I



II

LEGAL STATUS

[Date of request for examination] 22.12.1993
[Date of sending the examiner's decision of rejection] 25.02.1997
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number]
[Date of registration]

[Number of appeal against examiner's decision of rejection] 09-04638

[Date of requesting appeal against examiner's decision of rejection] 27.03.1997

[Date of extinction of right]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

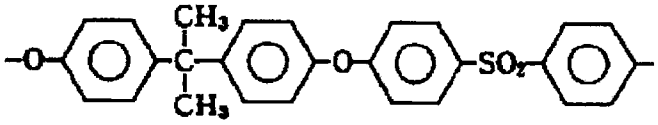
[Claim(s)]
[Claim 1] the solution which carried out the mixing dissolution of polysulfone system resin and the hydrophilic macromolecule -- this polysulfone system resin -- receiving -- a non-solvent -- or -- a swelling agent -- the art of the polysulfone system resin semipermeable membrane characterized by constructing a bridge in this hydrophilic macromolecule by performing radiation treatment to the polysulfone system resin semipermeable membrane which manufactured the system which added the additive as a film production undiluted solution.
[Claim 2] The art of the polysulfone system resin semipermeable membrane according to claim 1 whose hydrophilic giant molecule is a polyvinyl pyrrolidone or a polyethylene glycol.

[Translation done.]

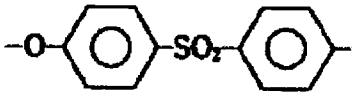
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the art of polysulfone system resin semipermeable membrane.
[0002]
[Description of the Prior Art] Conventionally, as a material of semipermeable membrane, many high molecular compounds, such as a cellulose acetate polyacrylonitrile polymethyl-methacrylate polyamide, have been used. On the other hand, although originally used as engineering plastics, since polysulfone system resin has the heat-resistant stability, acid-proof and alkali resistance and biocompatibility, and good resistance to contamination, it attracts attention as a semipermeable membrane material.
[0003] JP,58-104940,A etc. is conventionally proposed as an approach of obtaining the semipermeable membrane using polysulfone system resin in for example, journal OBU applied polymer Science (20 volumes, 2377-2394 pages, 1976) and (said 21 volumes, 1883-1900 pages and 1977). However, since this resin has too strong intermolecular cohesive force and blockades a surface hole and the internal hole which should be penetrated, control of hole formation becomes difficult. For this reason, only the thing with a as small and cut off molecular weight which also has small water permeability as [or less] 100,000 is obtained. On the other hand, the following means are proposed in recent years as an attempt which opens a big hole in a front face by the film using polysulfone system resin.
[0004] ** How to use the microfacies separation between different-species polymers. (JP,48-176,B, JP,54-144456,A, a 57-50506 official report, a 57-50507 official report, 57-50508 official report)
** How to have an extract and elution actuation after film production. (JP,54-26283,A, a 57-35906 official report, 58-91822 official report)
** How to produce a film in the state of metastable liquid distribution of a film production undiluted solution. (JP,56-154051,A, a 59-58041 official report, a 59-183761 official report, 59-189903 official report)
** How to put creativity at the time of spinning (JP,59-228016,A)
However, by the approach of **, it has come to obtain a 100,000 or more-cut off molecular weight big hole only by using the difference in the coagulation rate between polymers. In order to blend in large quantities moreover, the original good engine performance of polysulfone system resin is easy to be lost.
[0005] Moreover, the approach of ** is eluted, it is large and an extract and the inorganic granulation of blend polymer are classified into two approaches. In the former, although the polyethylene glycol and the polyvinyl pyrrolidone were main polymers, obtaining sufficient aperture and extract operation were difficult. In the latter example, silica powder is mixed, elution is carried out after film production by said JP,58-91822,A, using alkali, and it is 0.05 micrometers. Although it has succeeded in opening the above big hole, by this manufacture approach, the film which takes other pore size distribution from the same film production undiluted solution cannot be manufactured.

[0006] ** Just before an approach mixes the non-solvent or swelling agent of polysulfone system resin in large quantities to a film production undiluted solution and this film production undiluted solution carries out phase separation, it is a thing which it is and which produces a film by the way. By this approach, there is a fault which cannot use the temperature effect of a coagulation bath advantageously.
[0007] ** Although an approach is spraying the wind of high humidity at the time of film production and aperture expansion in this front face is realized, if there is the effectiveness only in one side and it results especially in a hollow fiber, by this approach, only the thing of the range where a cut off molecular weight is small is obtained.
[0008] Especially the semipermeable membrane that blended water-soluble polymers, such as a polyvinyl pyrrolidone, a polyethylene glycol, and polyvinyl alcohol, had the fault which can do only what has permeable low ability for the elution problem of this water-soluble polymer, and the swelling layer of this water-soluble polymer.
[0009]
[Problem(s) to be Solved by the Invention] this invention persons analyzed the above-mentioned fault, and as a result of inquiring wholeheartedly, they reached this invention. Especially, there is no elution of blend polymer and it aims at offering the art of polysulfone system resin semipermeable membrane for obtaining the very high semipermeable membrane of permeable ability.
[0010]
[Means for Solving the Problem] This invention has the next configuration. that is the solution which carried out the mixing dissolution of "polysulfone system resin and the hydrophilic macromolecule -- this polysulfone system resin -- receiving -- a non-solvent -- or -- a swelling agent -- by performing radiation treatment to the polysulfone system resin semipermeable membrane which manufactured the system which added the additive as a film production undiluted solution art of the polysulfone system resin semipermeable membrane characterized by constructing a bridge in this hydrophilic macromolecule. The film production undiluted solution used in order to manufacture polysulfone system resin semipermeable membrane in" this invention consists of 4 component systems which consist of polysulfone system resin (I), a hydrophilic macromolecule (II), a solvent (III), and an additive (IV) fundamentally. The polysulfone system resin (I) said here is usually a formula (1) or a formula (2).
[Formula 1]



(1)



(2)

Although it consists of a ********** unit, the functional group is included, or you may be the thing of an alkyl system and it does not limit especially.
[0011] A hydrophilic macromolecule (II) is a macromolecule which there are polysulfone system resin (I) and compatibility, and has a hydrophilic property. Although a polyvinyl pyrrolidone is the best and a denaturation polyvinyl pyrrolidone, a copolymerization polyvinyl pyrrolidone, polyvinyl acetate, a polyethylene glycol, etc. are mentioned to others, it is not limited to these.
[0012] Both solvents (III) are solvents which dissolve polysulfone system resin (I) and a hydrophilic macromolecule (II). Although the solvent of varieties, such as dimethyl sulfoxide, dimethylacetamide, dimethylformamide, a N-methyl-2-pyrrolidone, and dioxane, is used, dimethylacetamide, dimethyl sulfoxide, dimethylformamide, and a N-methyl-2-pyrrolidone are

especially desirable.
[0013] If an additive (IV) has a solvent (III) and compatibility, and serves as a good solvent of a hydrophilic macromolecule (II) and it becomes the non-solvent of polysulfone system resin (I), or a swelling agent, anything, it is good, for example, has water, a methanol, ethanol, isopropanol, a hexanol, 1,4-butanediol, etc. Considering a production cost, water is the most desirable. What is necessary is just to choose an additive (IV), after taking the freezing characteristic over polysulfone system resin (I) into consideration.
[0014] Easy for men of the same trade considers the combination which is arbitrary in each as for these combination, and has the above-mentioned property. Moreover, the mixed stock of two or more kinds of compounds is sufficient as a solvent (III) and an additive (IV).
[0015] As a presentation of this film production undiluted solution, polysulfone system resin (I) is 5 - 50 % of the weight that what is necessary is just the density range which can produce a film and has a property as film. In order to obtain high water permeability and a big cut off molecular weight, polymer concentration should be lowered and is 5 - 20 % of the weight desirably in this case. It becomes impossible to obtain sufficient viscosity of a film production undiluted solution, but to form the film at less than 5 % of the weight. Moreover, if 50 % of the weight is exceeded, it will be hard coming to form a through tube. In the case of a polyvinyl pyrrolidone, the thing of molecular weight 360,000, 160,000, 40,000, and 10,000 is marketed, as for especially the hydrophilic giant molecule (II), it is convenient to use this, but the thing of the other natural molecular weight may be used for it. However, as one of the reasons of addition of a hydrophilic macromolecule (II), for a certain reason, it is so little that the thickening effectiveness also uses the thing of the amount of macromolecules, is good, and an addition's can improve film production nature. One to 20% of the weight, although especially the addition of a polyvinyl pyrrolidone has 3 - 10 desirable % of the weight, it is influenced by the molecular weight of the polyvinyl pyrrolidone to be used. If film production nature is bad when molecular weight is too low, and polymer concentration is high and polymer molecular weight is too large when there are generally too few additions, washing after film production will become difficult. So, it also becomes one approach to mix that from which molecular weight differs, to carry out a role assignment, and to use.
[0016] The mixed dissolution of the two macromolecules is carried out above at a solvent (III). Although an additive (IV) is added here, since freezing characteristic is high for polysulfone system resin especially in the case of water, 1 - 5 % of the weight is especially preferably desirable one to 12% of the weight 15 or less % of the weight. When using an additive with small freezing characteristic, it is guessed easily that an addition increases. In this invention, since this 4th component is added, the amount of a hydrophilic macromolecule can be lessened.
[0017] Polysulfone system resin semipermeable membrane is obtained under the above conditions. Film production actuation should just use a well-known technique. About a flat film, this film production undiluted solution is flowed on a flat substrate, and it is immersed into a coagulation bath after that. About a hollow fiber, in order to maintain a hollow gestalt, infusion is used. although it is [spinning stability] better to use a thing lower than the high thing of freezing characteristic for infusion to a film production undiluted solution -- coagulation bath temperature and phase separation temperature, and a mouthpiece -- what is necessary is just to decide the best presentation suitably, since the smooth nature of a hollow fiber wall changes by correlation with temperature Hydrocarbons, such as the inactive Deccan octane undecane, may be used for polysulfone system resin. Moreover, a gas may be poured in and a hollow gestalt may be made to hold. Dry type length is 0.1-20cm, and 0.5-5cm is [spinning stability] still more desirable especially well. When a film is produced on the same presentation and the same conditions, the diameter of the hole which the flat film punctures on a front face from a hollow fiber tends to become large.
[0018] The polysulfone system resin semipermeable membrane obtained by this approach can improve water wettability by making a hydrophilic macromolecule remain in the film. However, when a residual hydrophilic-property macromolecule is water solubility, the elution of this hydrophilic macromolecule is not avoided and it has the fault [water permeability / of an

aperture / comparatively high] of being difficult to get again. This invention compensates this fault more than enough, is irradiating the radiation of extent with which polysulfone system resin's does not become transformation, deterioration, or practical use impossible about this polysulfone system semipermeable membrane obtained first, and carries out water insolubilization processing of the hydrophilic macromolecule by bridge formation. As long as this polysulfone system resin semipermeable membrane is the gestalt which can perform this processing regardless of a flat film and a hollow fiber, it may have what kind of gestalt. Moreover, radiation treatment here has the viewpoint of matter permeability to the most desirable gamma ray, although alpha rays, beta rays, a gamma ray, an X-ray, and an electron ray are raised.

[0019] It is most desirable to carry out gamma irradiation, after this semipermeable membrane has got wet in water especially about gamma ray processing in radiation treatment. As dosage, 0.5Mrad to 50Mrad(s) are desirable, and 0.5Mrad from a viewpoint of mechanical property maintenance of this semipermeable membrane to 10Mrad(s) are especially desirable.

[0020] In addition, based on the artificial organ criteria eluting material test method, the following evaluations were performed about the polysulfone system resin semipermeable membrane of this invention.

[0021] The solution which heated 0.5g of film with 50 cc of 70-degree-C warm water for 1 hour is the wavelength of 350-220 micrometers. UV absorption which can be set is 0.1 or less and 0.01NKMnO4. The consumption of 1.0ml or less of a water solution can be shown, and this trial can be passed.

[0022]

[Example] The following examples explain this invention to a detail further.

[0023] Hereafter, the used measuring method is as follows.

[0024] In the case of the permeable hollow fiber, this hollow fiber was inserted in the glass case which equipped both ends with the hole for ring current liquid, it produced the small module using the commercial potting agent, and measured permeable ability by the approach of computing from the amount of the water of fixed time amount which keeps at 37 degrees C, pours water pressure on the hollow filament inside, and is penetrated outside through the film, an effective film surface product, and the differential pressure between film.

[0025] The heating dissolution of the example 1 polysulfone 15 section, the polyvinyl-pyrrolidone (K90) 8 section, and the water 2.4 section was carried out at 80 degrees C at the dimethylacetamide 75 section. This film production undiluted solution turned into a cold melting mold undiluted solution which carries out phase separation at 65 degrees C. the mouthpiece which uses dimethyl sulfoxide / glycerol / polyvinyl-pyrrolidone (K30) =63/7/30 for infusion, and consists of an annular orifice with an outer diameter [of 1.0mm], and a bore of 0.7mm -- it breathes out out of a hole -- making -- a mouthpiece -- the coagulation bath which has water which kept it warm at 80 degrees C caudad installed 1.0cm from the field was passed, it rolled round to the skein after rinsing by the usual approach, and the hollow filament-like film was obtained. The mouthpiece kept it warm at 49 degrees C. When gamma irradiation processing of 2.5Mrad(s) was performed on this film, it was the absorbance 0.098 of permeable 4800 ml/hr/m2 / mmHg, and an effluent.

[0026] It was 730, when water permeability was measured without carrying out gamma irradiation processing of the hollow fiber of example of comparison 1 example 1. Moreover, the absorbance of an effluent was 1.58.

[0027]

[Effect of the Invention] If this invention is processed, there is no elution of the blended hydrophilic macromolecule and permeable, very high semipermeable membrane can be obtained. Furthermore, it can develop easily for the application as perfect dry film only by being immersed in water by ordinary pressure from the goodness of the water wettability which recovers permeable ability. Moreover, this effectiveness is maintained almost eternally.

[0028] To loading and dirt, since it is strong, the polysulfone system resin semipermeable membrane obtained by this processing can be used as a general industrial use way and blood

processing film of a medical field from a reverse osmotic membrane to high performance ultrafiltration membrane (or micro filter).

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号

特開平6－339620

(43)公開日　平成６年(1994)12月13日

(51)Int.Cl.[5]	識別記号	庁内整理番号	ＦＩ	技術表示箇所
Ｂ０１Ｄ　71/68		9153－4D		
Ｃ０８Ｊ　7/00	ＣＥＺ	7310－4F		
	３０５	7310－4F		

審査請求　有　発明の数１　ＯＬ　（全４頁）

(21)出願番号　特願平5－298075

(62)分割の表示　特願昭61－243176の分割

(22)出願日　昭和61年(1986)10月15日

(71)出願人　000003159
東レ株式会社
東京都中央区日本橋室町２丁目２番１号

(72)発明者　島垣　昌明
滋賀県大津市園山１丁目１番１号　東レ株式会社滋賀事業場内

(72)発明者　田中　和実
滋賀県大津市園山１丁目１番１号　東レ株式会社滋賀事業場内

(72)発明者　島村　政治
滋賀県大津市園山１丁目１番１号　東レ株式会社滋賀事業場内

(54)【発明の名称】　ポリスルホン系樹脂半透膜の処理方法

(57)【要約】

【構成】ポリスルホン系樹脂と親水性高分子を混和溶解した溶液に該ポリスルホン系樹脂に対して非溶媒もしくは膨潤剤なる添加剤を加えた系を製膜原液として製造したポリスルホン系樹脂半透膜に，放射線処理を施すことにより、該親水性高分子を架橋することを特徴とするポリスルホン系樹脂半透膜の処理方法。

【効果】本発明の処理を行なえば、ブレンドした親水性高分子の溶出がなく、透水性の極めて高い半透膜を得ることができる。さらに、常圧で水に浸漬するだけで透水性能を回復するその水濡れ性の良さから完全ドライ膜としての用途に容易に展開できる。また、この効果はほぼ永久的に持続される。

1

【特許請求の範囲】

【請求項1】ポリスルホン系樹脂と親水性高分子を混和溶解した溶液に該ポリスルホン系樹脂に対して非溶媒もしくは膨潤剤なる添加剤を加えた系を製膜原液として製造したポリスルホン系樹脂半透膜に，放射線処理を施すことにより、該親水性高分子を架橋することを特徴とするポリスルホン系樹脂半透膜の処理方法。

【請求項2】親水性高分子が、ポリビニルピロリドンもしくはポリエチレングリコールである請求項1記載のポリスルホン系樹脂半透膜の処理方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、ポリスルホン系樹脂半透膜の処理方法に関する。

【0002】

【従来の技術】従来、半透膜の素材としては、セルロースアセテート・ポリアクリロニトリル・ポリメタクリル酸メチル・ポリアミド等多くの高分子化合物が用いられてきた。一方、ポリスルホン系樹脂は、元来エンジニアリングプラスチックスとして使用されてきたが、その耐熱安定性、耐酸・耐アルカリ性、そして生体適合性、耐汚染性が良好であることから、半透膜素材として注目されている。

【0003】ポリスルホン系樹脂を用いた半透膜を得る方法として従来より例えば、ジャーナル・オブ・アプライド・ポリマー・サイエンス（20巻、2377～2394頁、1976年）及び、（同21巻、1883～1900頁、1977年）、特開昭58－104940号公報等が提案されている。しかし該樹脂は、分子間凝集力が強すぎて、表面の孔や貫通すべき内部の孔を閉塞してしまうため孔形成の制御が困難となる。このため、分画分子量が10万以下と小さくかつ透水性も小さいものしか得られていない。一方、近年、ポリスルホン系樹脂を用いた膜で、表面に大きな孔をあける試みとして、次のような手段が提案されている。

【0004】① 異種ポリマー間のミクロ相分離を利用する方法。（特公昭48－176号公報、特開昭54－144456号公報、同57－50506号公報、同57－50507号公報、同57－50508号公報）

② 製膜後、抽出・溶出操作を有する方法。（特開昭54－26283号公報、同57－35906号公報、同58－91822号公報）

③ 製膜原液の準安定液体分散状態で製膜する方法。（特開昭56－154051号公報、同59－58041号公報、同59－183761号公報、同59－189903号公報）

④ 紡糸時に工夫をこらす方法（特開昭59－228016号公報）

しかし、①の方法ではポリマー間の凝固速度の違いを利用しているのみで、分画分子量10万以上の大きな孔を得るに至っていない。その上、大量にブレンドするため、ポリスルホン系樹脂の本来の良好な性能が失われやすい。

2

【0005】また、②の方法は、ブレンドポリマーの抽出と無機顆粒を溶出する大きく2つの方法に分類される。前者においては、ポリエチレングリコール、ポリビニルピロリドンが主たるポリマーであるが、十分な孔径を得ることや抽出操作が困難であった。後者の例では、前記特開昭58－91822号公報で、シリカパウダーを混入して製膜後、アルカリを用いて溶出させ、0．05μm 以上の大きな孔をあけるのに成功しているが、この製造方法では同一製膜原液から他の孔径分布をとる膜を製造することはできない。

【0006】③の方法は製膜原液にポリスルホン系樹脂の非溶媒もしくは膨潤剤を大量に混合し、該製膜原液が相分離する直前のところで製膜するものである。かかる方法では、凝固浴の温度効果を有利に利用できない欠点がある。

【0007】④の方法は、製膜時に高湿度の風を吹きつけることで、該表面での孔径拡大を実現しているが、該方法では片面にしかその効果はなく、特に中空糸膜に至っては、分画分子量は小さい範囲のものしか得られない。

【0008】特に，ポリビニルピロリドン，ポリエチレングリコール，ポリビニルアルコール等の水溶性ポリマーをブレンドした半透膜は，該水溶性ポリマーの溶出問題や，該水溶性ポリマーの膨潤層のため，透水性能が低いものしかできない欠点を有していた。

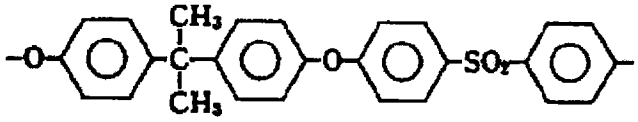
【0009】

【発明が解決しようとする課題】本発明者らは、上記欠点を解析し、鋭意検討した結果本発明に到達した。特に、ブレンドポリマーの溶出がなく，透水性能の極めて高い半透膜を得るための、ポリスルホン系樹脂半透膜の処理方法を提供することを目的とする。

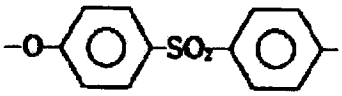
【0010】

【課題を解決するための手段】本発明は次の構成を有する。すなわち、「ポリスルホン系樹脂と親水性高分子を混和溶解した溶液に該ポリスルホン系樹脂に対して非溶媒もしくは膨潤剤なる添加剤を加えた系を製膜原液として製造したポリスルホン系樹脂半透膜に，放射線処理を施すことにより該親水性高分子を架橋することを特徴とするポリスルホン系樹脂半透膜の処理方法。」本発明においてポリスルホン系樹脂半透膜を製造するために用いる製膜原液は、基本的にはポリスルホン系樹脂（I）、親水性高分子（II）、溶媒（III）および添加剤（IV）からなる4成分系で構成される。ここで言うポリスルホン系樹脂（I）は、通常式（1）、または式（2）

【化1】



(1)



(2)

の繰り返し単位からなるものであるが、官能基を含んでいたり、アルキル系のものであってもよく、特に限定するものではない。

【００１１】親水性高分子（II）は、ポリスルホン系樹脂（Ｉ）と相溶性があり、かつ親水性を持つ高分子である。ポリビニルピロリドンが一番良く、他に変性ポリビニルピロリドン、共重合ポリビニルピロリドン、ポリ酢酸ビニル、ポリエチレングリコール等が挙げられるが、これらに限定されるものではない。

【００１２】溶媒（III ）は、ポリスルホン系樹脂（Ｉ）及び親水性高分子（II）を共に溶解する溶媒である。ジメチルスルホキシド、ジメチルアセトアミド、ジメチルホルムアミド、Ｎ－メチル－２－ピロリドン、ジオキサン等多種の溶媒が用いられるが、特にジメチルアセトアミド、ジメチルスルホキシド、ジメチルホルムアミド、Ｎ－メチル－２－ピロリドンが望ましい。

【００１３】添加剤（IV）は、溶媒（III ）と相溶性を持ち、親水性高分子（II）の良溶媒となり、かつ、ポリスルホン系樹脂（Ｉ）の非溶媒又は膨潤剤となるものであれば何でも良く、例えば、水、メタノール、エタノール、イソプロパノール、ヘキサノール、１，４－ブタンジオール等がある。生産コストを考えると水が最も望ましい。添加剤（IV）は、ポリスルホン系樹脂（Ｉ）に対する凝固性を考え合わせた上で選択すれば良い。

【００１４】これらのおのおのの組合せは任意であり、上記の性質をもつ組合せを考えるのは、同業者にとって容易なことである。また、溶媒（III ）・添加剤（IV）は、２種類以上の化合物の混合系でも良い。

【００１５】該製膜原液の組成として、ポリスルホン系樹脂（Ｉ）は、製膜可能でかつ膜としての特性を有する濃度範囲であれば良く、５～５０重量％である。高い透水性、大きな分画分子量を得るためにはポリマー濃度は下げるべきで、この場合望ましくは５～２０重量％である。５重量％未満では、製膜原液の十分な粘度を得ることができず、膜を形成できなくなる。また、５０重量％を越えると貫通孔を形成しにくくなる。親水性高分子（II）は、特にポリビニルピロリドンの場合、分子量３６万、１６万、４万、１万のものが市販されており、これを使うのが便利であるが、もちろんそれ以外の分子量（II）の添加の理由の１つとして増粘効果もあるため、添加量は高分子量のものを用いるほど少量で良く、製膜性を向上できる。ポリビニルピロリドンの添加量は、１～２０重量％、特に３～１０重量％が望ましいが、用いるポリビニルピロリドンの分子量に左右される。一般に添加量が少なすぎる場合、分子量が低すぎると製膜性が悪く、またポリマー濃度が高く、ポリマー分子量が大きすぎると、製膜後の洗浄が困難となる。それ故、分子量の異なるものを混合して役割分担して用いるのも一つの方法となる。

【００１６】以上２つの高分子を溶媒（III ）に混合溶解する。ここへ、添加剤（IV）を添加するが、特に水の場合、ポリスルホン系樹脂にとって凝固性が高いため、１５重量％以下、好ましくは１～１２重量％、特に１～５重量％が望ましい。凝固性が小さな添加剤を用いるときは添加量が多くなることは容易に推測される。本発明では、この第４成分が、添加されるため、親水性高分子の量を少なくすることができる。

【００１７】以上の条件のもとでポリスルホン系樹脂半透膜が得られる。製膜操作は、公知技術を用いれば良い。平膜については、該製膜原液を平坦な基板上に流展し、その後凝固浴中に浸漬する。中空糸膜については、中空形態を保つため、注入液を用いる。注入液は、製膜原液に対して凝固性の高いものより、低いものを用いた方が紡糸安定性は良いが、凝固浴温度・相分離温度・口金温度との相関で中空糸膜内壁の平滑性が変化するので、適宜最良組成を決めれば良い。ポリスルホン系樹脂に不活性なデカン・オクタン・ウンデカン等の炭化水素を用いても良い。また気体を注入して中空形態を保持させてもよい。乾式長は０．１～２０cmであり、特に０．５～５cmが紡糸安定性も良く、さらに望ましい。同一組成、同一条件で製膜した場合、中空糸膜より平膜の方が表面に開孔する孔の直径は大きくなる傾向がある。

【００１８】かかる方法で得たポリスルホン系樹脂半透膜は、膜中に親水性高分子を残存させることによって、水濡れ性を改善することができる。しかし残存親水性高分子が水溶性の場合、該親水性高分子の溶出が避けられず，かつ，また，孔径の割りに高い透水性を得難いという欠点を有している。本発明は，この欠点を十二分に補

スルホン系樹脂が，変型，変質，または実用不能にならない程度の放射線を照射することで、架橋による親水性高分子の水不溶化処理をするものである。該ポリスルホン系樹脂半透膜は、平膜，中空糸膜を問わずかかる処理を行なえる形態であれば，いかなる形態を有していてもかまわない。また，ここでいう放射線処理とは，α線，β線，γ線，X線，電子線があげられるが，物質浸透性の観点から，γ線が最も望ましい。

【００１９】放射線処理で特にγ線処理については，該半透膜が水に濡れた状態でγ線照射するのが最も好ましい。線量としては，０．５Ｍｒａｄから５０Ｍｒａｄが好ましく，特に該半透膜の機械的特性保持の観点から，０．５Ｍｒａｄから１０Ｍｒａｄが好ましい。

【００２０】なお、本発明のポリスルホン系樹脂半透膜について、人工臓器基準溶出物試験法に基づき、以下の評価を行なった。

【００２１】膜０．５ｇを７０℃温水５０ccで１時間加熱した溶液は、波長３５０～２２０μｍ におけるＵＶ吸収が０．１以下、０．０１NKMnO$_4$ 水溶液の消費量１．０ml以下を示し、該試験に合格することができる。

【００２２】

【実施例】以下の実施例によって本発明をさらに詳細に説明する。

【００２３】以下、用いた測定法は次のとおりである。

【００２４】透水性

中空糸膜の場合は、両端に環流液用の孔を備えたガラス製のケースに該中空糸膜を挿入し、市販のポッティング剤を用いて小型モジュールを作製し、３７℃に保って中空糸内側に水圧をかけ膜を通して外側へ透過する一定時間の水の量と有効膜面積および膜間圧力差から算出する方法で透水性能を測定した。

【００２５】実施例１

ポリスルホン１５部、ポリビニルピロリドン（Ｋ９０）８部、水２．４部をジメチルアセトアミド７５部に８０℃で加熱溶解した。この製膜原液は、６５℃で相分離する低温溶解型原液となった。注入液にジメチルスルホキシド／グリセリン／ポリビニルピロリドン（Ｋ３０）＝６３／７／３０を用いて、外径１．０㎜、内径０．７㎜の環状オリフィスからなる口金孔内から吐出させ、口金面から１．０㎝下方に設置した８０℃に保温した水を有する凝固浴に通過させ、通常の方法で水洗後カセにまき取り、中空糸状膜を得た。口金は４９℃に保温した。該膜に２．５Ｍｒａｄのγ線照射処理を行ったところ、透水性４８００ml/hr/m^2 /㎜Hg 、溶出物の吸光度０．０９８であった。

【００２６】比較例１

実施例１の中空糸膜をγ線照射処理しないで透水性を測定すると７３０であった。また、溶出物の吸光度は、１．５８であった。

【００２７】

【発明の効果】本発明の処理を行なえば、ブレンドした親水性高分子の溶出がなく、透水性の極めて高い半透膜を得ることができる。さらに、常圧で水に浸漬するだけで透水性能を回復するその水濡れ性の良さから完全ドライ膜としての用途に容易に展開できる。また、この効果はほぼ永久的に持続される。

【００２８】この処理により得られたポリスルホン系樹脂半透膜は、目づまり、汚れに対して強いため、逆浸透膜から、高性能限外濾過膜（あるいは精密濾過膜）まで、一般産業用途及びメディカル分野の血液処理膜として使用することができる。